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Piedmont field laboratory at Charlottesville

The Waste Sulphite Material of Paper Mills as an Adjuvant to Certain Spray Materials

By R. H. HURT

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The Piedmont Field Laboratory

A picture of the Piedmont field laboratory appears on the front cover page. One corner of the insectary is shown at the left of the main building. The laboratory is a substantial structure 26 feet by 30 feet, with a full basement; and the insectary is 12½ feet by 36 feet. These structures provide very convenient facilities for experiments and investigations bearing upon insect pests and diseases of orchard fruits.

This laboratory was made possible through the generous donation of $2,500 for this purpose by fruit growers in this region; also by an appropriation from the General Assembly of Virginia to cover the remainder of the cost of the structures and necessary equipment for the laboratory. The University of Virginia cooperated in the project by granting permission for the laboratory to be located on its grounds. The laboratory was constructed in 1930.

The Waste Sulphite Material of Paper Mills as an Adjuvant to Certain Spray Materials[1]

By R. H. Hurt, *Assistant Plant Pathologist* [2]

Introduction

The object of this bulletin is to discuss in a brief way the properties and use of the waste by-product of paper and pulp mills which is known as lignin or sulphite pitch.

There are three methods used to secure fiber, or cellulose, from trees; namely, the sulphite, soda, and sulphate processes. The method of extraction employed in any particular case, however, depends upon the kind of wood to be extracted and the purpose for which the fiber is intended to be used. The most widely used method, however, is the sulphite process and the waste by-product derived from this process is the one in which we are mainly interested.

In the sulphite process of extraction of fiber, spruce, hemlock and balsam logs, after being reduced to chips in large chipping machines, are cooked in a solution containing lime and sulphur in a combination known as calcium bisulphite. In the calcium bisulphite solution there is a quantity of sulphur dioxide which plays an important part in the cooking process. The fiber made by this process is called sulphite pulp.

In the soda process of extraction, poplar and other woods of a similar nature are digested with a caustic soda solution. This solution is strongly alkaline which is directly opposite in reaction to the sulphite solution which is acid. Due to the type of wood used and the solution in which the wood is cooked, the waste by-product material from the soda process of extraction is unfit for use of any kind in connection with spraying or spray materials. In the first place, this waste material carries very little soapy material and is strongly alkaline in reaction. Furthermore, the manufacturers using this process have a recovery method by which the spent soda liquor is evaporated to dryness, the residue burned, and the alkali materials which entered into the original extracting liquid are thereby recovered.

The sulphate pulp is made by the sulphate process which is a modification of the soda process. The cooking liquid is a mixture of caustic soda and sodium sulphite. The name "sulphate" is derived from the addition of sodium sulphate at a certain stage in the process. Wood, such as pine and other resin-

[1] Paper No. 78 from the Department of Botany and Plant Pathology.

[2] Acknowledgment is hereby made to Mr. B. C. Moomaw, Covington, Virginia, for his kindly assistance in securing material for experimentation.

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ous wood, is used in this process. Due to the nature of the wood, the waste by-product derived from this process contains a fairly high percentage of soapy material which is of more value as a spreading and emulsifying agent than the material derived from the soda process. This sulphate waste, however, is very much inferior to the sulphite waste material as an emulsifying agent and as a wetting and sticking material. The manufacturers using the sulphate process also have a recovery method by which at least a part of the chemicals going into the original cooking solution are recovered for further use in fiber extraction.

Lignin Pitch or Sulphite Waste

The waste sulphite material known as lignin or sulphite pitch is the only one of the waste by-products of fiber extraction which is of interest to the fruit grower. This material occurs on the market as a brown powder and also as a dark syrup-like liquid and is sold under various trade names which are given elsewhere in this bulletin.

No doubt the greatest loss to paper and pulp manufacturers, using the sulphite process for fiber extraction, is the waste liquor of the pulp mills. The non-fibrous portion of the wood which is dissolved in the cooking process constitutes approximately 50 per cent of the original material. Consequently 50 per cent of the wood extracted by this process is wasted so far as the finished pulp or paper is concerned. It has been roughly estimated that between 4 and 5 billion pounds of this waste material is lost each year in the United States and Canada.

Here, then, is an example of waste that is a real challenge to science, for the paper industry is eagerly waiting for scientists to discover a method by which this waste material can be converted into a valuable by-product. Krimmel [1] in 1924 pointed out that work on this problem had produced some results but that the real solution was still to be found. He mentions, however, that grain alcohol, dyestuffs, medicinals, and explosives may be made from the waste sulphite liquor but at high cost and in small quantities. It may also be used for other purposes, such as a binder, fuel, and in fire-extinguisher compounds. It also finds extensive use in tanneries because it contains a fairly high percentage of tannin. However, the most recent discovery regarding this waste product and the one that promises to aid materially in its solution is the discovery that this waste material can be used as an emulsifying agent for making oil emulsions and as a sticker and spreader for certain spray materials.

Chemical Composition of Lignin Pitch

The lignin pitch material occurs on the market in two forms as previously stated. After the calcium bisulphite liquor has been spent as an extracting

[1] Maximilian A. Krimmel: Chemistry in the Pulp and Paper Industry. Chemistry in Industry. 1925. 2nd ed., page 250. New York City: The Chemical Foundation, Inc.

solution, it is drained off and stored in tanks where lime is usually added to neutralize its acidity. The spent liquor is then placed in large evaporating tanks and evaporated down to a heavy, syrupy liquid, or else the evaporation is continued until all of the water is driven off, leaving a brown residue of solid material. This residue is then powdered and stored in water-proof bags.

The chemical composition of the two forms of lignin pitch is approximately the same, the only difference being in the fact that the liquid form contains about 50 per cent water by weight whereas the other form is dry. The chemical analyses given below were furnished through the courtesy of two different manufacturers, and represent two different sources of the material.

Analyses of the Liquid and Powdered Forms of Lignin Pitch

	Liquid	Powder
Total solids	51.00	98.00
Moisture	49.00	2.00
Ash	5.78	11.16
Total organic and volatile	99.22	88.84
Silica and insoluble	.04	.08
Iron (Fe)	.016	.03
Lime (CaO)	3.13	6.00
Magnesia (MgO)	.81	1.60
Total alkalies (as Na_2O)	.04	.09
Total sulphur	3.15	6.25

Analysis of Powdered Form from a Different Source

Total solids	97.49
Soluble solids	97.05
Insoluble solids	.44
Non-tannins	48.94
Tannin	2.51
Ash	7.80

In the above analyses the soapy type of material which gives this product its emulsifying properties as well as its wetting and spreading qualities is not indicated except under the head of organic and volatile matter. This lignin pitch material in either powdered or liquid form contains considerable resinous, soapy material which accounts for its valuable properties as an adjuvant to certain spray materials. The slight variations which occur in the chemical analyses of the various brands of lignin pitch are of very little importance so far as the value of the material for use in spray materials, or as an emulsifying agent for oil emulsion, is concerned.

Properties and Use of Lignin Pitch

Research has shown that the sulphite waste material, lignin pitch, can satisfactorily replace calcium caseinate, or similar emulsifying agents, as an emulsifier for making cold mix oil emulsion. In fact, this material, in either form, is the best and cheapest emulsifying agent for making cold mix oil emulsions now available.

Oil emulsions made with lignin pitch, either the powder or liquid, are miscible in any proportion with lime-sulphur solution, with the soluble sulphurs which are now on the market, and also with Bordeaux mixture. The lignin pitch emulsions are very stable and will withstand very low temperatures before breaking down. It has been found that these emulsions may be stored for an indefinite period of time if properly made. But if they are to be stored for a long period of time, they should be put in wooden containers; however, they may be stored for six months or a year in steel drums without danger of deterioration.

Formulas and Directions for Preparing Lignin Pitch Emulsions
(In three separate quantities)

Formula A

Oil	2 gallons	50 gallons	54 gallons
Water	1 gallon	25 gallons	27 gallons
Powdered lignin pitch	4 ounces	6 pounds	6¼ pounds

Formula B

Oil	2 gallons	50 gallons	54 gallons
Water	1 gallon	25 gallons	27 gallons
Liquid lignin pitch	6 fl. oz.	1 gallon	1¼ gallons

Stock emulsions made according to the above formulas contain 66⅔ per cent oil and 33⅓ per cent water. Each 1½ gallons of the stock emulsion carries 1 gallon of oil. Therefore, in order to determine the amount of stock solution required for any given percentage of oil wanted in 100 gallons of water or spray solution, multiply the percentage of oil wanted by 1½. For example, if a 3 per cent oil solution is wanted, multiply 3 by 1½ which will give 4½ gallons, the amount of stock solution required for each 100 gallons of water to make a 3 per cent oil spray.

In preparing an emulsion with either the liquid or powdered material the procedure is the same. The proper amount of water is measured out and poured into the spray tank or other container in which the emulsion is to be made. The lignin pitch material is then measured (in case of the liquid) or weighed (in case of the powder) and added directly to the water in the spray tank. The agitator is then started and run for a few minutes in order to thoroughly mix the emulsifier and water. After this has been accomplished, the pump is started and the oil gradually added while the mixture is pumped back on itself in the tank. The way in which the oil is added largely determines the type of emulsion which results in the finished product. The oil may be added when using lignin pitch just as it is added when calcium caseinate and other emulsifiers of this type are used. The proper way, however, to add the oil to the spray tank, regardless of whether lignin pitch or calcium caseinate is being used as the emulsifier, is to add it slowly until all of the oil has been added. A very good way to add oil to a spray tank for

making stock emulsion is to roll the barrel onto the tank and place it so that the small bung will allow the oil to flow from the barrel into the tank while the sprayer is running. The flow of the oil from the small bung is just about as fast as the oil should be fed into the tank. While the oil is being fed, or poured, into the tank the pump should be running and a pressure of 200 to 300 pounds maintained. The total mixture should pass through the pump at least twice. If this procedure is followed a bad emulsion will rarely, if ever, result, and it will assure a stock emulsion which will stand up indefinitely under ordinary conditions.

There are two types of emulsions which are possible with oil and water, one is an oil-in-water type and the other is a water-in-oil type. The former will mix with water and is the type which is used for spraying. The latter will not mix with water, but will mix with oil, and is unsuited for spraying purposes. Occasionally in preparing the cold mix oil emulsion, using either calcium caseinate or lignin pitch, the water-in-oil type of emulsion will result. This is called a reversed emulsion. A reversed emulsion may be caused by several factors, namely, by adding the oil too rapidly to the emulsifier and water, by using too small a quantity of the emulsifier, and by trying to make the emulsion when the water and oil are very cold. If, for any reason, the water-in-oil or reversed type of emulsion results, it may be converted to a good emulsion by adding more water and re-pumping the mixture. Sometimes just a few gallons of water will suffice to change a bad emulsion into a good one if the mixture is re-pumped. Any extra water added must be taken into account so that the correct amount of the stock emulsion will be added to the spray tank in order to maintain the proper percentage of oil in the diluted spray.

The lubricating oils used in experimental trials with lignin pitch as the emulsifier were oils commonly used by fruit growers for making the cold mix oil emulsion; namely, Diamond Paraffin Oil, Junior Red Engine Oil, Nabob Oil, and Lybra Oil. Any lubricating oil, however, may be emulsified with lignin pitch. If very heavy oils, those ranging from 250° to 300° in viscosity, are to be emulsified, slightly more of the lignin pitch material should be used than is recommended in the regular formulas. The heavy oils are somewhat harder to emulsify than the lighter ones, but fruit growers will rarely, if ever, have an occasion to emulsify oils heavier than 250° in viscosity.

Extensive field tests were made by the writer and by fruit growers during the 1929 season. Several large orchards were sprayed in 1929 with the cold mix oil emulsion made with lignin pitch. The lignin pitch material, in both liquid and powdered form, was recommended in the 1930 Virginia Spray Calendar for making the cold mix oil emulsion, and was used extensively for this purpose in Virginia and adjoining states. The results of these field tests have shown that an emulsion of this type is just as efficient and safe to use as

those made with calcium caseinate or similar emulsifiers, and are more stable and easier to handle.

Powdered Lignin Pitch as a Spreader and Sticker for Dry Mix Sulphur-Lime

Powdered lignin pitch has been found to be a very good spreading and wetting agent for dry mix sulphur-lime, and consequently is a splendid substitute for calcium caseinate in this spray material. The following dry mix formula has been found to be very satisfactory under Virginia conditions:

Dusting sulphur	50 pounds
Hydrated lime	42 pounds
Powdered lignin pitch	8 pounds

In preparing dry mix according to the above formula, or any other formula for that matter, a good grade of dusting sulphur and the best available hydrated lime should be used. The ingredients should be thoroughly mixed in a dust mixer or a barrel mixer and screened through a 14- to 16-mesh screen. By thorough screening, the small lumps of sulphur are broken up, a job that is not easily accomplished in any other way. The ingredients may also be mixed in a box with a shovel or hoe, but this method of mixing is not entirely satisfactory and is not recommended when any other type of mixer is available. If a good grade of dusting sulphur and a high grade hydrated lime are used in combination with the powdered lignin pitch material as the wetting and sticking agent, a dry mix material will be obtained which possesses excellent wetting and sticking qualities. The sticking qualities of any dry mix depends largely upon the fineness of the sulphur and the quality of the hydrated lime used, and the thoroughness in which these ingredients are mixed.

The dry mix sulphur-lime spray may be used on either peaches or apples as a summer fungicide. This material, however, has not been used very generally in Virginia as an apple spray. A dry mix spray made from good quality materials makes a splendid non-caustic spray for varieties of apples which are not very susceptible to apple scab. Dry mix, generally, is not quite as efficient as lime-sulphur, calcium sulphide, or Bordeaux mixture for apple scab control in severe scab seasons.

Dry mix made according to the formula given above should be used at the rate of 8 pounds to each 50 gallons of water as a peach fungicide, and at the rate of 10 pounds to 50 gallons of water when used on apples. During seasons in which apple scab is especially severe, 12½ pounds of the dry mix material may be used to each 50 gallons of water.

Dry mix sulphur-lime made with powdered lignin pitch as the wetting and sticking agent was tested on a rather large scale during the season of 1929 in several York Imperial apple orchards. Due to the favorable results obtained

with this formula of dry mix in 1929, its use was extended in 1930 when a good many growers purchased it through their local spray dealers. The writer also conducted experiments with the lignin pitch dry mix in 1930. The material was compared with the calcium caseinate dry mix formula, Koloform, and dry lime-sulphur on apples, and with calcium caseinate dry mix on peaches. The results of these tests, together with those obtained by growers, indicate that dry mix made with powdered lignin pitch as the wetting and suspending agent is equally as efficient in its fungicidal value as the calcium caseinate dry mix; and in addition is cheaper to prepare, easier to handle, and has better suspension qualities.

Other Suggested Uses for Lignin Pitch

Where nicotine sulphate, or black leaf 40, is being used in a water solution, lignin pitch in either form makes an excellent wetting and spreading agent for the nicotine. When used as a wetting agent for nicotine sulphate, 1 pound of powder or 1 quart of the liquid should be used for each 50 gallons of water. If this material is used in the nicotine solution, no soap is necessary because the lignin pitch material contains a fairly high percentage of soapy material which gives it splendid wetting and spreading properties.

The material is also suggested as a suspending agent for lead arsenate and lime-sulphur solution. Where agitation is poor, the material in either form will help a great deal in holding the lead arsenate and lime in suspension and will check to some extent the chemical reaction between lime-sulphur and lead arsenate. It is not recommended, however, as a panacea against this chemical reaction. In using this material with lime-sulphur, not more than 1 pound of the powder, or 1 quart of the liquid, should be used for each 50 gallons of spray solution. The lignin pitch has some slight fungicidal value and in using it the user is not adding a material which will act as a medium for the growth of bacteria or fungi. However, it is not recommended in spray materials for any purpose other than its suspending and wetting properties. The material has some slight caustic properties when used in large quantities either alone or in combination with other materials. However, it will require 15 to 20 pounds of this material in 200 gallons of spray solution to cause injury. It may be seen from this statement that the recommended amounts in the various combinations are entirely safe.

Sources of Supply

No doubt the lignin pitch material is sold by all manufacturers who use the sulphite process in pulp extraction, but the writer is not familiar with any sources other than those herein listed. It may be obtained through local spray dealers, or from the following manufacturers: (1) Robeson Process Company, 230 Park Avenue, New York, under trade names, Goulac and Glutrin; (2)

International Paper Company, 100 East 42nd Street, New York, under trade names, Bandarene flour and Bandarene liquid; (3) Champion Fiber Company, Canton, North Carolina, under trade names, Bindex powder and Bindex liquid; and (4) Brown Company, Berlin, New Hampshire, as waste sulphite liquor.

Summary

1. The material designated in this bulletin as lignin pitch, or sulphite pitch, is the waste sulphite material derived by digesting lignin of wood with calcium bisulphite liquor. The material is sold under various trade names as indicated in the text.

2. The different brands of this material are about the same in chemical composition and other properties. The slight differences in composition that may occur should be of little importance so far as their value as emulsifiers and suspending agents is concerned.

3. The lignin pitch material, in either liquid or powdered form, is the best and cheapest emulsifying agent available at the present time. Emulsions made with this material are very stable and will withstand very low temperatures without breaking down. They are also miscible in any proportion with lime-sulphur solution, soluble sulphur, and Bordeaux mixture.

4. The powdered form of lignin pitch is an excellent wetting and suspending agent for dry mix sulphur-lime. It may be substituted weight for weight for calcium caseinate in the preparation of dry mix sulphur-lime, but the quantity indicated in the formula given in the text has been found most efficient in this preparation.

5. In using lignin pitch in spray solutions, it has been found that 1 pound of the powder or 1 quart of the liquid to each 50 gallons of solution is sufficient as a suspending and wetting agent. As much as 2 pounds of the powder and 2 quarts of the liquid may be used in each 50 gallons of spray solution without injury; however, it is rarely, if ever, necessary to use this amount.